A STUDY OF THE DECAY OF NALED (DIBROM) RESIDUES ON GRAPE FOLIAGE AND SOIL IN KERN COUNTY, CALIFORNIA AUGUST 1975

By

Keith T. Maddy, Staff Toxicologist
Charles S. Kahn, Agricultural Inspector
A. Scott Fredrickson, Agricultural Chemist

HS-345

California Department of Food and Agriculture
Division of Pest Management, Environmental
Protection and Worker Safety
Worker Health and Safety Branch
1220 N Street, Sacramento, California 95814

A STUDY OF THE DECAY OF NALED (DIBROM) RESIDUES ON GRAPE FOLIAGE AND SOIL IN KERN COUNTY, CALIFORNIA AUGUST 1975

By
Keith T. Maddy, Staff Toxicologist;
Charles S. Kahn, Agricultural Inspector;
A. Scott Fredrickson, Agricultural Chemist
Agricultural Chemicals and Feed
California Department of Food and Agriculture
1220 N Street
Sacramento, California 95814

INTRODUCTION

Naled is a low toxicity organophosphate insecticide-acaricide. It has an acute oral LD_{50} (rat) of 430 mg/kg and an acute dermal LD_{50} (rabbit) of 1100 mg/kg. It is used to control leafhoppers, aphids, mites and many other insects on a wide variety of crops. Over 57,931 pounds of naled were reported as applied to 52,000 acres of grapes in 1975 in California. Since it is not a restricted material and most of it is applied by growers, these figures understate its usage considerably. Naled is marketed as liquids, dusts and emulsifiable concentrates.

Dibrom 8 Emulsive (Chevron Chemicals 239-1281 AA), used in this study, contains 8 pounds of naled per gallon of concentrate. This label recommends 1/2-2/3 pints per acre in 100 gallons of water with a 24-hour worker reentry interval and a 4-day preharvest interval on grapes. Dibrom 4 Dust (Chevron Chemicals 239-1220 AA), also used in this study, is 4 percent naled by weight. Label recommendations for grapes are 20 to 50 pounds of Dibrom with a 4-day preharvest interval. Worker safety regulations in California require a one-day worker reentry interval for naled on grapes.

APPLICATION

Dibrom was applied to two vineyards at the following rates:

Field 1: Dibrom 8 Emulsive 1 pt/10 gal of water/acre (55 acres)

Field 2: Dibrom 4 Dust 30 lb/acre (17 acres)

Both fields were treated by aerial application. The grapes were approximately 4 weeks from harvest.

SAMPLING

Triplicate samples were collected 6 and 25.5 hours post-application in Field 1 and 1 hour post-application in Field 2.

The leaf samples consisted of approximately 100 leaf punches, each 2.5 cm. in diameter. Duplicate samples were analyzed for penetrated and surface residue while the third was analyzed for total residue.

Soil was sampled by collection of 50 small plastic spoonfuls of surface dust collected each time about one foot from the base of the grape plant. Samples were collected from near plants along a diagonal line across the field. The final sample weighed approximately 100 grams.

ANALYTICAL METHODS (Extraction from Foliage)

The procedure used for the extraction of dislodgeable, penetrated, and total residues from leaf punches was originally published by Gunther in "The Bulletin of Environmental Contamination and Toxicology", 9, 243-249, 1973. It has been documented several times in detail, with modifications by our laboratory that were made to accommodate the various pesticides and their metabolites.

The sample container and leaf punches are weighed and the gross weight recorded.

Total Residues

1. The leaf punches are transferred to a blending jar. The empty sample container is again weighed and the net weight of the punches recorded.

2. Approximately 50 gms of sodium sulfate and 100 mls of ethyl acetate are added.

3. The sample is blended at high speed for 3 minutes, keeping the blender cup cool by immersing it in a container of cool water. The blender cup is removed and the sample allowed to settle.

4. An aliquot is decanted into a teflon-capped bottle and stored in the freezer prior to clean up and analysis.

Dislodgeable Residues

1. Fifty mls of water and approximately 4 drops of Sur-Ten solution (1:50) are added to the sample containers. The containers are capped and placed in a multi-purpose rotator and rotated at 30 cycles/min. for 60 min. The aqueous solution is decanted through a glass wool plug into a 500 ml separatory funnel.

2. The punches are rotated a second time, using 50 mls of water and 4 drops of Sur-Ten solution, for 30 min. This is added to the first extraction.

3. The sample is then hand-shaken for approximately 10 secs with 30 mls of water. The container is drained into the separatory funnel with the first two extractions.

4. The aqueous solution is extracted three times with 50 ml of ethyl acetate. The solvent is filtered through sodium sulfate into a glass stoppered mixing cylinder and the volume is recorded. The solvent is mixed in the cylinder. An aliquot is decanted into a teflon-capped bottle and stored in the freezer prior to clean up and analysis.

Penetrated Residue

1. After the last water rinse is drained for the dislodgeable residue, the punches are transferred to a blender jar. The emply container is weighed and the net weight of the punches recorded.

2. Approximately 50 gms of sodium sulfate and 100 mls of ethyl acetate are added.

3. The sample is blended and handled the same as the total residue sample.

ANALYTICAL METHODS (Extraction From Soil)

1. Finely divide soil sample to remove or break up lumps. Air dry if muddy.*

2. Add 10 percent water by weight; mix well.

3. Extract with a 2:1:1 petroleum ether: ethyl ether: acetone mixture. Use the maximum amount that is compatible with the sample container. (There must be free liquid over the soil.)

4. Place on jar rotator or shaker for 1 hour.

5. Filter an aliquot for instrument analysis. Concentrate if needed.*

*Dibrom degrades rapidly with some appearing as DDVP.

The concentrate of DDVP in Dibrom analytical grade standards has been known to range up to 30 percent, due probably to aging and degradation.

Storage of both standards and samples is critical. Ambient storage of standards of Dibrom resulted in a 13 percent decrease in potency over a 9-day period as compared to a frozen standard. Ambient storage of a 2.0 ng/μl standard resulted in a total loss of the Dibrom peak in that same 9-day period, while a refrigerated standard, 2.0 ng/μl, lost 50 percent of its strength as compared to a freshly made standard.

Extracted samples refrigerated overnight may also show a loss of Dibrom. Initial analysis showed about 2-3 ppm, the next day only traces of Dibrom remained.

Due to the volatility of these chemicals, any attempts at concentration steps should be thoroughly checked out.

ANALYTICAL METHODS (Chromatography)

Varian 2700, FPD detector, standard flows, 6' x 2 mm of 3 percent OV-101 (2) 160^{o}, 45 psi head pressure.

Retention times:	DDVP	0.5 min.
	Dibrom	3.0 min.

RESULTS

Weather conditions for the study period are recorded in Table 1. Average maximum and minimum temperatures were 94.0 and 68.5°F, respectively. There was some precipitation 1 day prior to the study.

Results of the study are recorded in Table 2 and Figure 1. Twenty-four hours after application, surface naled residue levels were approximately 1.8 and surface DDVP was about 0.78 ppm. Total naled remained above 7 ppm 24 hours after application. Soil residues of naled dropped below 0.05 ppm in 24 hours.

TABLE 1: DAILY TEMPERATURE AND PRECIPITATION

Date (1975)	TEMPERATURE (°F) Maximum	Minimum	Precipitation (Inches)
8-19	87	66	Trace
8-20	93	71	
8-21	96	66	
8-22	100	71	
Average	94.0	68.5	Total Trace

TABLE 2: NALED RESIDUES ON GRAPE LEAVES IN KERN COUNTY

Field 1 -

Date (1975)	Sample Interval	Surface Residue (PPM) DDVP	Naled	Penetrated Residue (PPM) DDVP	Naled	Total Residue (PPM) DDVP	Naled
8-20	6 hrs	4.7	10.5	0.9	<0.5		
8-20	6 hrs	6.8	19.8	1.5	<0.5		
8-20	6 hrs					10.4	19.4
8-21	25-1/2 hrs	0.7	1.1	0.5	<0.5		
8-21	25-1/2 hrs	0.7	1.9	0.6	<0.5		
8-21	25-1/2 hrs					1.0	6.9

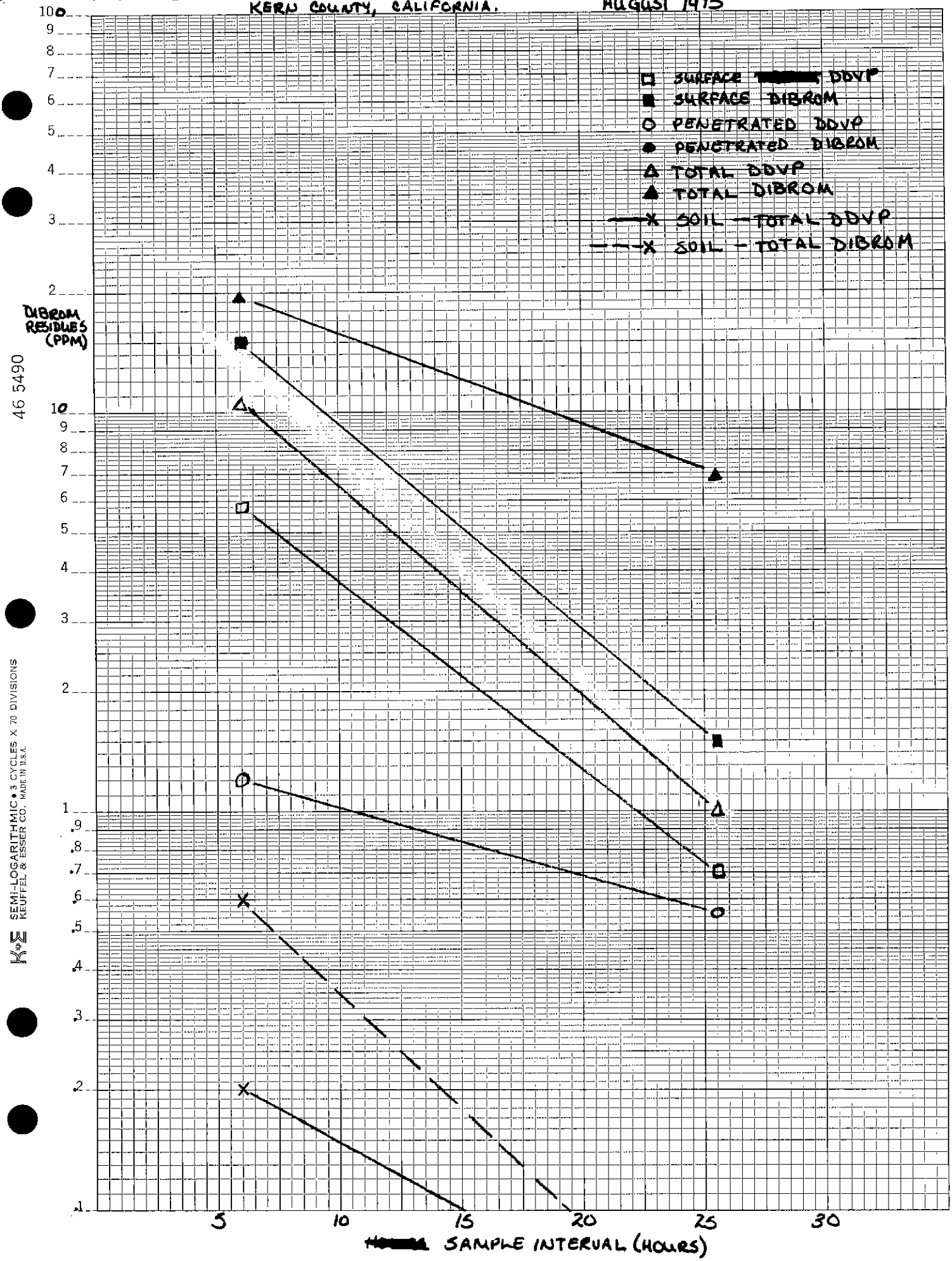
Field 2 -

Date (1975)	Sample Interval	Surface Residue (PPM) DDVP	Naled	Penetrated Residue (PPM) DDVP	Naled	Total Residue (PPM) DDVP	Naled
8-21	1 hr	1.4	1.8	0.2	<0.5		
8-21	1 hr	0.9	2.4	0.2	<0.5		
8-21	1 hr					1.1	0.9

TABLE 3: NALED RESIDUE IN SOIL FROM VINEYARDS IN KERN COUNTY

Date	Sample Interval	Field #	Total Residue (PPM) DDVP	Naled
8-20	6 hrs	1	0.2	0.6
8-21	25-1/2 hrs	1	< 0.05	< 0.05
8-21	1 hr	2	0.1	0.4

FIGURE 1: DIBROM RESIDUE ON GRAPE FOLIAGE AND SOIL IN FIELD 1
KERN COUNTY, CALIFORNIA. AUGUST 1975



46 5490

SEMI-LOGARITHMIC • 3 CYCLES X 70 DIVISIONS
KEUFFEL & ESSER CO. MADE IN U.S.A.